

EFFECT OF HEAT ON THE FLAVORING COMPONENTS OF MAPLE SIRUP: A Preliminary Study by Gas Chromatography

SUMMARY: Portions of a distinctively flavored commercial maple sirup were heated by autoclaving at 15 psig (250°F) for 1.5 and 4 hr. A GLC flavor profile of the treated and untreated sirups showed that 25 components in their flavor fractions changed in relative amounts. In the light colored original sirup, acetol and compounds related to lignin (vanillin, syringaldehyde, dihydroconiferyl alcohol) predominated. As the sirup was heated, carbohydrate breakdown products began to appear and then to predominate (acetol, furanones, cyclotene, and HMF). As the carbohydrate degradation products increased the sirup darkened in color and became acrid in flavor; at this point vanillin began to decrease. From this preliminary study it would seem possible, after identifying all the compounds in the profile, to produce various levels of different flavor in maple sirup by a regulated heat process. The need is indicated for a complete study of the production of maple flavorants by heat, starting with a flavorless sap concentrate.

INTRODUCTION

THE CHARACTERISTIC flavor of maple sirup is developed during the concentration of the maple sap by atmospheric boiling (Skazin, 1930). Low temperature vacuum evaporation produces an almost flavorless sirup (Findlay and Snell, 1935; Porter et al., 1952). Early efforts to identify the chemical compounds in maple sirup contributing to its flavor were handicapped by the lack of present day methods of isolating and identifying trace amounts of flavorants. Nelson (1928), Skazin (1930), and Skazin and Snell (1928-29) have reported by classical methods the isolation of an aldehyde with a vanillin odor. Sair and Snell (1939) advanced somewhat the knowledge of maple flavorants by using chloroform to isolate the flavoring compounds from the sugars and ash constituents of maple sirup. However, this work was also limited by the techniques available for separation and identification. A vanillin-like compound was isolated but not definitely identified.

Underwood et al. (1961) attempted to extend the chloroform extract work of Sair and Snell using column chromatography; vanillin and syringaldehyde were definitely found along with evidence of many more compounds. However, it was not until the advent of gas chromatography that real progress began to be made in unraveling the secret of maple flavor. During the 1960's the author and co-workers reported on a large number of compounds found in maple sirup related to its flavor (Filipic et al., 1965; Filipic et al., 1969; Underwood and Filipic, 1963). As an accumulative result of these studies a GLC procedure was designed (Underwood et al., 1969) to produce a chromatogram depicting maple flavor (flavor profile). 25 peaks on this chromatogram represent flavorants in a chloroform extract of sirup. Other work (Willits and Porter, 1950) had revealed that the

flavor can be enhanced in commercial maple sirup by additional heat treatment. The flavor changes in that work was evaluated by organoleptic and color measurements.

Using the GLC flavor profile, it is possible to determine changes in the individual flavorants with varying sirup treatments. This paper reports a preliminary study on component changes in the chloroform flavor extract of a commercial maple sirup given additional heat treatment.

EXPERIMENTAL

A TYPICAL commercial maple sirup with distinctive maple flavor was divided into three portions. The first portion was held without treatment; the second autoclaved for 1.5 hr at 15 psig (250°F), and the third autoclaved for 4 hr. A ½ gal aliquot of each portion was extracted with chloroform as described earlier (Underwood et al., 1969). These three extracts were analyzed by the GLC procedure detailed in the same paper to produce flavor profiles for the

three portions of sirup. Reproductions of these profiles are shown in Figures 1, 2, and 3. A semi-quantitative evaluation of the changes in amounts of the compounds in the flavor extract in significant amounts is shown in Table 1.

RESULTS & DISCUSSION

A COMPARISON of Figures 1, 2, and 3 shows that most of the components increased as the sirup was heated. The semi-quantitative data in Table 1 showing these trends in more detail, indicate that a few compounds decreased rather than increased. Only half of the peaks recorded in the table are named, because not all of them were completely identified. Since a milder extraction was used in this study than in the exhaustive study reported earlier (Filipic et al., 1969), fewer peaks were obtained and identification procedures in addition to retention time had to be repeated. Only those peaks deemed useful to evaluate the effect of the heat treatment were completely reidentified by mass spectrographic analysis, but the heat treatment produced unpredicted changes in some peaks. Therefore, a further, more complete study of the effect of heat on maple flavorants, using the flavor profile, will require complete identification of all the peaks on the chromatogram.

The exhaustive extraction of chloroform soluble flavorants from maple sirup mentioned above has shown that these compounds can be divided into two

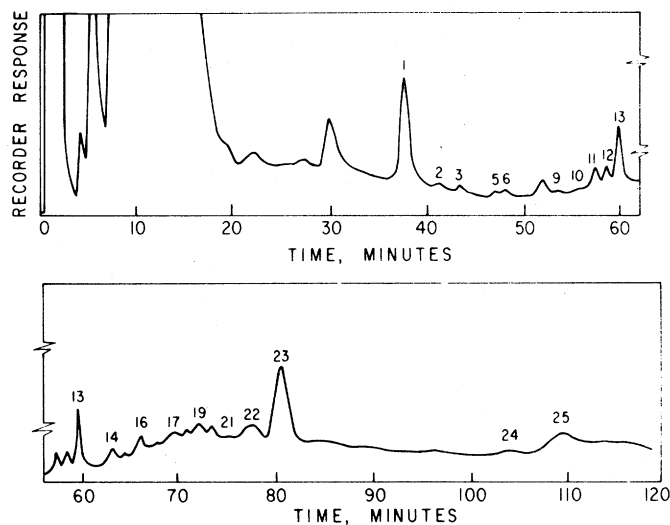


Fig. 1—Flavor profile of a typical commercial maple sirup.

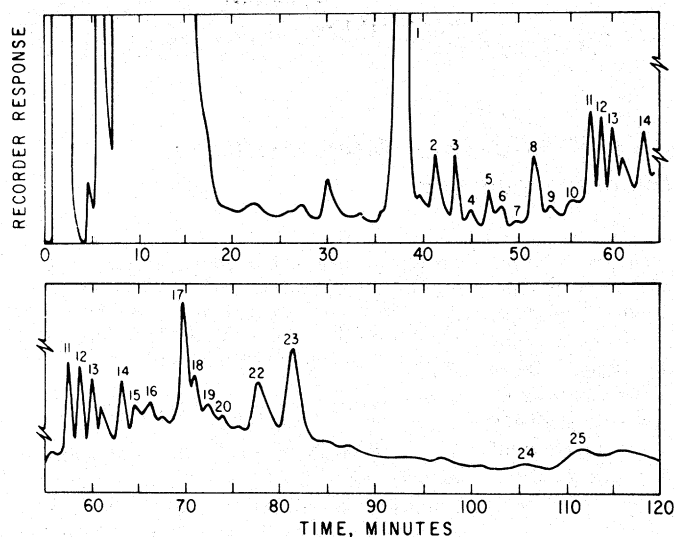


Fig. 2—Flavor profile of a typical commercial maple sirup autoclaved 1.5 hr at 15 psig.

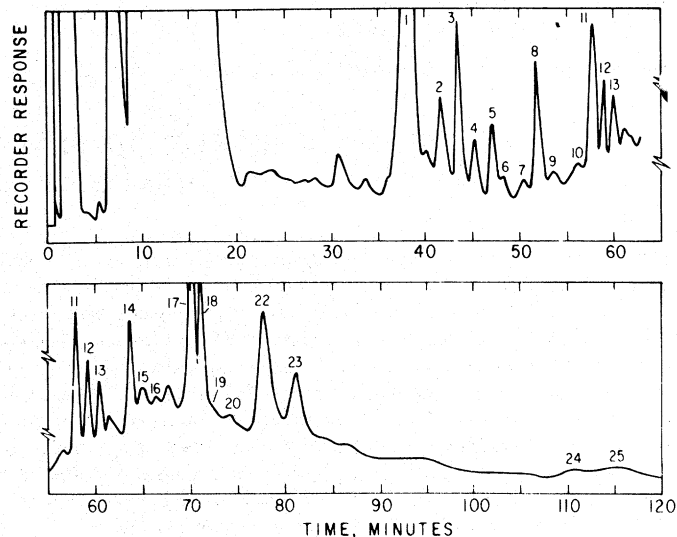


Fig. 3—Flavor profile of a typical commercial maple sirup autoclaved 4.0 hr at 15 psig.

groups according to their source. These sources are the trace of a ligneous material and the carbohydrates (almost 100% sucrose) in the sap.

Vanillin was the only measured compound of definite ligneous origin in the

extract. It was probably the predominant flavorant in the original sirup. The further heat treatment caused a modest increase in the amount of this constituent at the end of 1.5 hr, but after 4 hr a significant decrease had occurred. The identity of

the other compounds which decreased must be reaffirmed to determine whether other ligneous compounds respond as vanillin does.

Acetol is a major constituent in flavor extracts of maple sirup and was increased by the heat treatment. Its role in the formation of maple flavor compounds is yet unknown. Undoubtedly its increased production is from monosaccharides resulting from hydrolysis of the sucrose in the sirup. Also, Table 1 indicates that the rate of acetol formation decreases as the time of heating increases. This is probably due to the fall in pH of the sirup from the build-up of acids as the heating continues. Acetol formation from a hexose such as glucose is favored by an alkaline media (Lento et al., 1960).

The BHT (peak 13) found in this extract comes from the diethyl ether used to purify the original chloroform extract. Looked upon at first as a nuisance in our work, we now use it as an internal standard for rating the uniformity of our final concentrate of flavorants.

Finally, Table 1 lists a number of compounds that are formed from the carbohydrates in the sap and sirup. Sucrose constitutes 95% of the total solids in the exudate of the maple tree. The compounds shown make from an entirely negative to a heavily positive contribution to the desirable maple flavor in the sirup. Isomaltol and cyclotene have flavor characteristics that would help build a pleasing maple flavor. These both increased significantly during the heat treatment, especially the cyclotene. This increase in cyclotene is highly important because it is reportedly a powerful flavoring agent.

Two furanones have been identified in maple sirup. They are the "pineapple" furanone (2,5 dimethyl-4-hydroxy-3(2H)

Table 1—Peak heights^a of components of maple sirup flavor extract.

Peak no.	Identity	Heating time—hours			
		0	1.5	4	
		Peak ht.	Peak ht.	Peak ht.	% Increase
1	Acetol	68	976	1224	1700
2		2.0	37	49	2350
3	Acetic acid	3.5	42	113	3128
4	Furfural	—	7.5	31	—
5	Propionic acid	2.5	25	48	1820
6		3.5	6.0	4	14
7		1.5	0.5	8	430
8		1.5	42	83	5400
9	Isomaltol	0.5	4.0	6.0	1100
10		1.0	5.5	1.5	50
11	Cyclotene	10.0	56	88	780
12		9.5	50	33	247
13	BHT ^b	34	36	37	9
14	Pineapple furanone	8.5	36	66	676
15		1.5	11	10.5	600
16		9.5	10	4	—58
17	α -Furanone	2.0	71	300	14,900
18		4.0	13	—	—
19		5.5	6	—	—
20		5.0	4.5	4	—10
21		1.0	1.5	1.5	50
22	HMF	8.5	30	77	800
23	Vanillin	47	56	34	—28
24	Syringaldehyde ^c				
25	Dihydroconiferyl alcohol ^c				

^aIn millimeters.

^bArtifact introduced by diethyl ether treatment of extract.

^cPeaks too low and broad for heights to have any significance.

furanone), and a second furanone as yet not definitely identified. The mass spectrographic data of the latter appears to conform to the structure 4-hydroxy-2-hydroxymethyl-5-methyl 3(2H) furanone reported by Shaw et al., 1968. The "pineapple" furanone has strong caramel flavoring characteristics and certainly contributes to maple flavor, although probably modifying the more delicate flavor in an extremely fancy maple sirup to give it caramel tones. Its formation slowed with heating time and, again, this is probably due to fall in pH. The second furanone showed a large rate of increase with heating and probably contributes to the heavy caramel flavor of the middle grades of sirup.

The acids, furfural and HMF all increase with heating. These compounds impart the heavy, acrid caramel flavor to lower grade, dark, sirups. When sirups were heated at temperatures higher than reached in this study, as is possible in a heat exchanger (Willits et al., 1966), the predominant compound that forms is hydroxymethylfurfural (HMF) (Porter et al., 1952). The increase in acidity that accompanies heating causes accelerated production of HMF until the flavor imparted by this and other compounds to the sirup makes it unpalatable.

The study has answered one question

that has been debated by those involved in maple sirup flavor research. Earlier work had demonstrated definitely that total flavor in maple sirup increases with heat treatment and changes in character. The flavor changes from the delicate maple to a heavy acrid caramel flavor, the latter over-riding the true maple. It has not been known whether true maple flavorants continue to increase but are masked by the relatively larger increase of the other flavorants, or the production of maple flavorants is limited. The brief data in this work indicate that there is a limit to the increase of maple flavorant and continued heating will cause a decrease. Proper regulation of heat and heating time would be required to produce a sirup of optimum maple flavor. This was discussed on a practical basis by Willits et al. (1966) in reporting on a heat process for continuously increasing the flavor in maple sirup.

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